

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION.



## An Improvement in the Manufacture of Cellulose Acetate.

We, KODAK LIMITED, a British Company, of 61-65, Kingsway, London, W.C.2, Assignees of CARL JOHAN MALM, a citizen of Finland, of Kodak Park, Rochester, County of Monroe, State of New York, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This process relates to an improvement in the manufacture of cellulose acetate by which a cellulose acetate exceptionally free from haze is produced.

In the manufacture of cellulose acetate, many types of cellulose are used as raw materials for the acetylation. In all commercial forms of these types, there are small amounts of mineral salts, and while an attempt is made thoroughly to remove these and other impurities from the cellulose material, before acetylating it, it is difficult to extract the last traces of them. Nevertheless, in the production of cellulose acetate, which is to be used in the manufacture of photographic films, and like transparent objects, it is important that these last traces should be removed. Even minute quantities of such impurities in the finished cellulose ester, may develop a haze which will render the material of little or no use in photography.

According to the invention this haze is readily avoided in the cellulose acetate by treating the finished dope (that is, the cellulose acetate which has been hydrolysed to the desired acetyl content) in the hydrolysing bath with hydrochloric acid. This added acid probably reacts with the mineral salts, such as the metallic sulphates or mixtures of sulphates and phosphates or other organic or inorganic salts which may have been formed by the action of the acetylating bath upon the vessel containing it or which have been present in the cellulosic materials used, the reaction of the hydrochloric acid making these salts more readily water-soluble, so that they are removed from the cellulose acetate when this is subsequently precipitated and washed.

[Price 1/-]

It is well known in this art that the addition of a strong hydrochloric acid solution to a cellulose acetate dope will hydrolyse the ester very rapidly from chloroform solubility to acetone solubility, and even farther, with such rapidity that it is next to impossible to control the reaction. It is, no doubt, for this reason that proposals have been made to add only a small proportion of hydrochloric acid, sometimes under 1 per cent. of the weight of the acetylation bath, in the course of the hydrolysis of the primary acetate to secondary acetate, the hydrolysis being then continued for several hours.

In the present invention the hydrochloric acid is not used as an aid to the hydrolysis but is added at the end of the usual hydrolysis step and just prior to precipitating the cellulose acetate. Sufficient time, of course, must be allowed for complete dispersion of the hydrochloric acid throughout the hydrolysing bath. Ordinarily, in the manufacture of batches up to 100 pounds of finished dope, the hydrochloric acid may be added to the bath about one-half hour prior to precipitation, the mass being vigorously stirred during that one half-hour; this allows sufficient time for thorough intermingling of the acid. Furthermore, generally a concentration of not more than 1 per cent. of hydrochloric acid, based on the weight of the reacting solution, will give the desired results in the time indicated. A smaller proportion of the hydrochloric acid may be used, provided the concentration be adequate to render the metallic salts sufficiently soluble. If much more than 1 per cent. of hydrochloric acid is added, the acid appears to attack deleteriously the cellulose ester and otherwise affects the product and it is, therefore, not advisable to increase the concentration greatly above this percentage unless the temperature be sufficiently lowered to render hydrolytic action on the cellulose acetate negligible. The hydrochloric acid is conveniently added in the form of a solution, preferably of about 10 per cent. strength in acetic acid.

Even with optimum amounts of the

added acid, it is desirable to lower the temperature of the hydrolysing bath before the hydrochloric acid is added. This lowered temperature decreases the hydrolytic effect of the hydrochloric acid while apparently it does not markedly reduce its interaction with the metallic salts present in the solution, whereby their solubility in water is increased. It is desirable, therefore, to maintain the temperature during this time at or about 20° C. The temperature may be higher, especially if smaller batches are used where the hydrochloric acid can be more readily dispersed throughout the mass, thus preventing any local over-heating.

The addition of the hydrochloric acid at the beginning of the hydrolysis is objectionable, for while the haze in the solution at first becomes less marked, on continued action, to the end of the hydrolysis, an increase in haze is produced so that the finished cellulose acetate is apt to contain more haze than if there had been no hydrochloric acid treatment.

The following specific Example illustrates the invention.

To 100 parts by weight of a cellulose acetate dope which has been prepared by any of the well-known acetylation processes and has been hydrolysed to the desired content of acetyl are added 2 parts of hydrochloric acid of 35 per cent. strength diluted with 5 parts of acetic acid. The temperature of the dope is preferably lowered to approximately 20° C. prior to the addition of the hydrochloric acid. After thorough mixing for approximately one-half-hour, the mass is precipitated into a bath of water containing 35-40 per cent. of acetic acid, and subsequently washed and dried. The cellulose acetate thus formed, when dissolved in acetone containing suitable plasticisers and coagulated upon a film-forming sur-

face by the evaporation or other removal of the acetone from the dope, gives a brilliant, transparent film, entirely free from haze.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1) In the process of manufacturing cellulose acetate, the step which comprises mixing hydrochloric acid with the hydrolysing bath containing the cellulose acetate which has been hydrolysed to the desired acetyl content. 55

2) In the step referred to in claim 1, adding the hydrochloric acid in solution in acetic acid. 60

3) In the step referred to in claim 1, adding the hydrochloric acid in the form of a solution of about 10 per cent. strength in acetic acid. 65

4) In the process of manufacturing cellulose acetate, the step which comprises adding to the cellulose acetate which has been hydrolysed to the desired acetyl content in the hydrolysing bath approximately  $\frac{1}{2}$  per cent. of hydrochloric acid, based on the weight of the total contents of the hydrolysing bath. 70

5) In the process of manufacturing cellulose acetate, the step which comprises adding to 100 parts of a hydrolysing bath, containing cellulose acetate which has been hydrolysed to the desired acetyl content, 2 parts of hydrochloric acid of 35 per cent. strength diluted with 5 parts of acetic acid, whereby a cellulose acetate free from haze is obtained. 80

Dated this 25th day of July, 1930.

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